

The Phase Rule and its application

Thermodynamics

A system:

Some portion of the universe that you wish to study

The surroundings:

The adjacent part of the universe outside the system

closed system: only exchange of mechanical and thermal energy, no mass exchange

open system: exchange of energies and mass

phase: is a physically distinct part of a system that is mechanically separable from other parts in the system;
e.g. a melt or a mineral

Thermodynamics

A phase diagram:

P, T Shows the stability ranges of phases (minerals, melts, solutions)

as functions of composition,, pH and Eh.

Components: Minimum number of chemical constituents that

are required to describe the compositions of all phases in the system

(there are never be more components than phases in a system)

Degrees of freedom: The number of variables to define the position of a mineral assemblage in a phase diagram

Extensive properties: V, m, partial

pressure

Intensive properties: P, T, pH, Eh (Environmental variables)

The Phase Rule

$$F = C - P + v$$

F = # degrees of freedom

C = number of variables to define

P = position of a mineral assemblage in a phase diagram

P = number of phases

Phases are mechanically separable constituents

C = minimum # of components (chemical

constituents that must be specified in order to define all phases)

v = intensive properties or environmental variables

v in P/T and pH/Eh diagrams = 2

Variables

- Extensive Variables – dependent on the amount of material present
 - mass
 - volume
 - moles of atoms
- Intensive Variables – independent on the amount of material present
 - pressure
 - temperature
 - density
 - compositional proportions

Gibbs Phase Rule rewritten

$$F = C - P + 2$$

F – number of degrees of freedom of intensive variables (p, t, x) that will still preserve chemical equilibrium

C – number of components (chemical entities)

P – number of phases (minerals, volatiles)

Phase Equilibrium

For a heterogeneous system in equilibrium

$$F = C - P + 2$$

F = number of degree of freedom

C = number of components

and P = number of phases

Phase : Any homogenous, physically distinct and mechanical separable portion of a system which is separated from other such part of a system by definite boundary surface.

Phase Equilibrium

A system may contain one or more than one phase

i) A system containing only liquid water is a one phase

system or $P = 1$

ii) a system containing liquid water and water vapor is a two phase system or $P = 2$

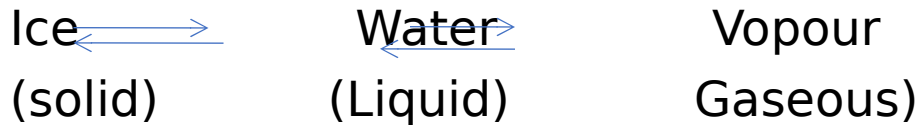
iii) A system containing ice, liquid water and water vapor is a three phase system or $P = 3$

Component: The minimum number of independent phase can be expressed either directly or in form of chemical equation, negative or zero sign being permitted.

Phase Equilibrium

Examples:

i) Water system consists of equilibrium



It is a one component system because the composition of the three phases can be expressed as water.

ii) Sulphur System consists of four phases- monoclinic(s), Rhombic(s), liquid(l) and vapours(g) is also one component system

iii) Decomposition of CaCO_3 by heat can be expressed



Phase Equilibrium

There are three different constituents forming three different phases. But the composition of each phase can be expressed in terms of two of constituents.

Degree of Freedom:

the smallest number of independently variables such as pressure , temperature and concentration that can be varied without disturbing the number of phases present in equilibrium

For examples:

i) Ice ,water and vapour system: This system has no degree of freedom or in other word it is invariant i.e. $F=0$

Phase Equilibrium

ii) Water – Vapour system: This system has only one degree

of freedom or in other words, it is invariant i.e. $F=1$.

ii) For a gas : This system has two degree of freedom or it is

bi variant.

Equilibrium:

A system is said to be in equilibrium if the

properties like temperature, composition etc of various phases do not under go any change with time. These equilibrium may be of two types

True Equilibrium: Which is obtained from either direction

Phase Equilibrium

pressure and 0°C is a true equilibrium

Metastable Equilibrium : a state of system which can be obtained only from one direction and too very careful change of conditions. For e.g. Water at -2°C .

Derivation of Gibbs Phase Rule:

The degree of freedom , F of a system

is given by the difference of total number of variables required to specify the system and number of independent equations available to define the system at equilibrium. Thus

Degree of freedom = Total number of variables - Number of variables defined by the system because of its being in equilibrium

Phase Equilibrium

A simple phase containing C components can be completely

by defined by C-1 concentration terms.

For P phase having C components then the number of concentration required will be $P(C-1)$. Besides concentration variables, there are two more variables i.e. temperature and pressure of the system

Thus total number of variables = $P(C-1) + 2$ ii

For a system of three phases , two equation are required to

define each component.

Phase Equilibrium

For a system having P phase, $P-1$ equations are required for each component. If there are C component present in P phases, then

The number of independent equations + C ($P-1$)iii

Putting equation (ii) and (iii) in equation (i), we get

$$F = [P(C-1) + 2] - [C(P-1)]$$

$$F = C - P + 2$$

Phase Equilibrium

Phase Diagrams :

The diagram representing conditions of temperature, pressure and composition at which one or more phase exist together.

Application of Phase Rule to One component system:

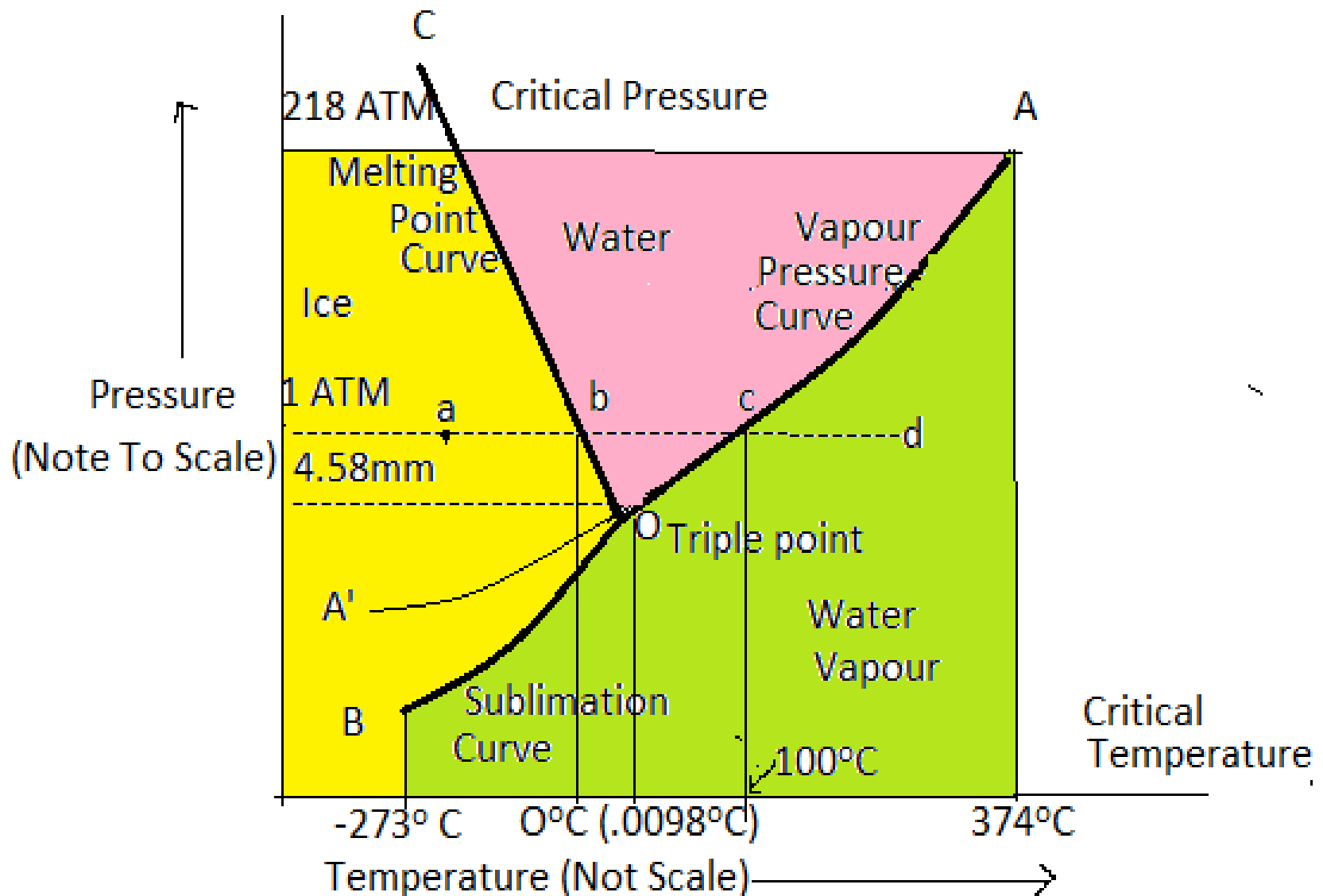
As $C=1$ and minimum $P=1$ therefore maximum $F=C-P+2=2$

The two degree of freedom chosen on the plot are temperature versus pressure

A. Phase Diagram of Water System:

Phase diagram of water as shown in fig

Phase Equilibrium



Phase Equilibrium

Some important features of Water System:

(i) **Possible phases** : Ice (s), Water(l), Vapour (g)

(ii) **Curves**: three stable curves (a) OA (Vapour pressure curve, Water $\rightleftharpoons$ Vapour)

(b) OB (Sublimation Curve, Ice $\rightleftharpoons$ Vapour)

(c) OC (Melting point curve, Ice $\rightleftharpoons$ Water)

iii) **One metastable curve** OA' (Vapour pressure curve of super cooled water)

(iv) **Areas** : Three areas representing ice, water and vapour.

Phase Equilibrium

(v) Triple point (O):

Where all the three phases are in equilibrium (0.0098°C and 4.58 mm pressure).

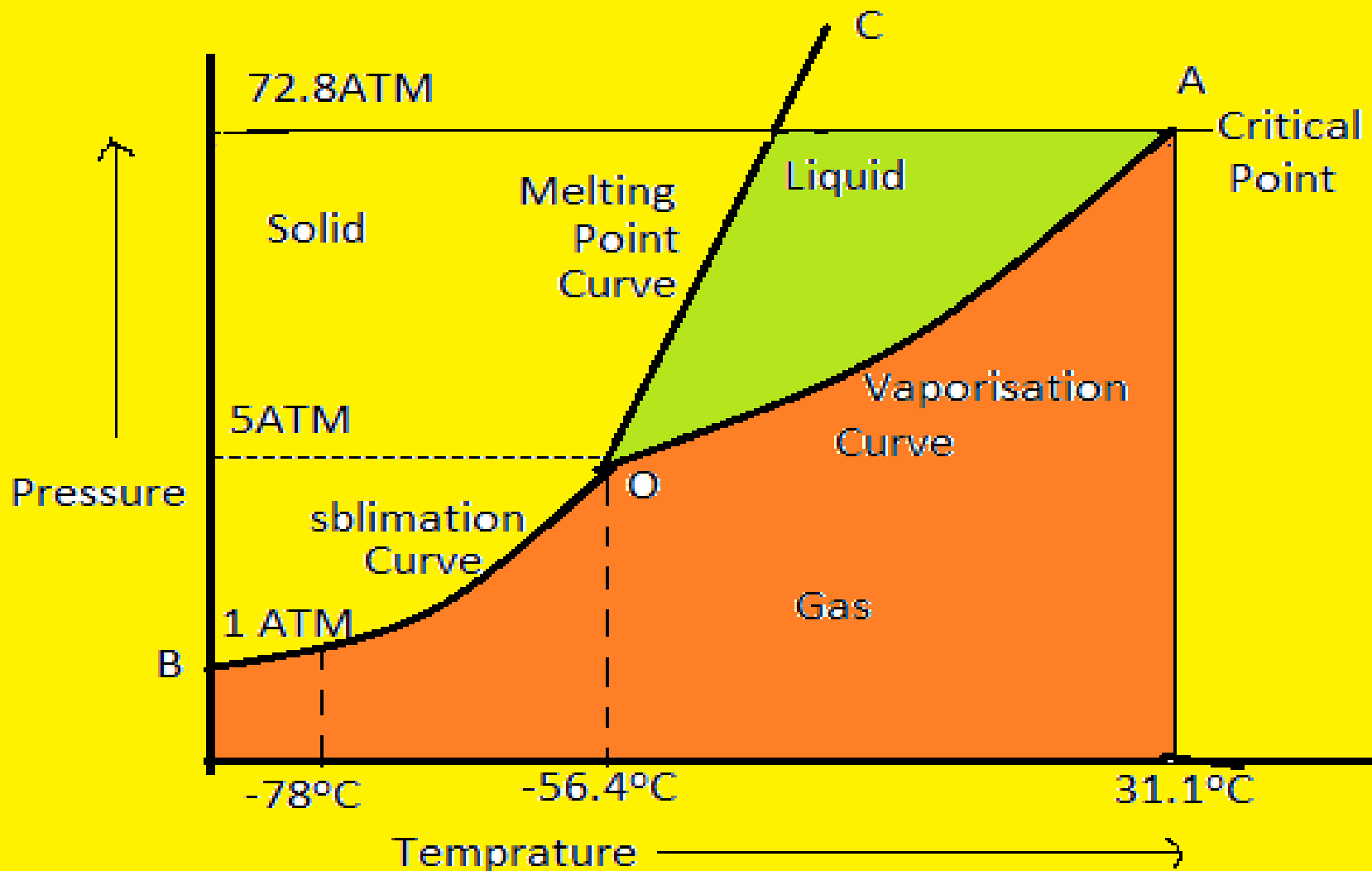
The melting point curve OC slopes towards pressure axis

has negative slope, showing that the melting point of ice

decreases with increase of pressure

Phase Equilibrium

B. Phase Diagram Of Carbon dioxide System:



Phase Equilibrium

Phase diagram of Carbon dioxide:

Some Important Features :

(i) **Possible phases:** Solid CO₂, liquid CO₂ and gases CO₂

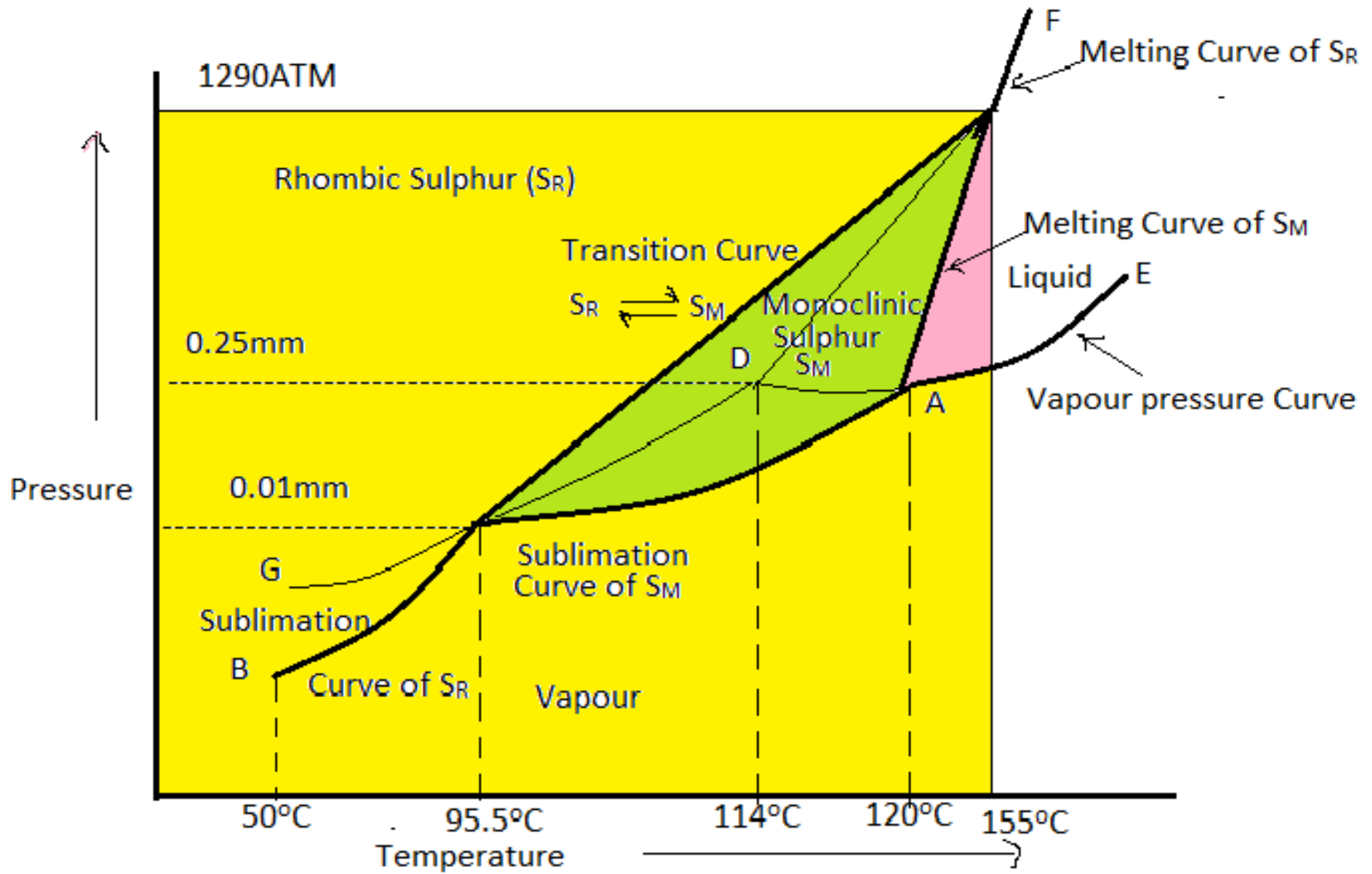
(ii) **Curves:** Three stable curves OA(vaporization curve), OB(sublimation curve) and OC (melting curve).

(iii) **Areas:** Three areas representing solid CO₂, liquid CO₂ and gases CO₂ respectively.

(iv) **Triple point(O):** Where all the three phases exist together(-56.4° C and 5 atm pressure)

Phase Equilibrium

C. Phase Diagram Of Sulphur System :



Phase Equilibrium

Sulphur system (one component system):

Some Important Features:

(i) **Possible phases:** Rhombic Sulphur (S_R), monoclinic Sulphur (S_M), Sulphur vapour (S_V) and Sulphur liquid (S_L).

(ii) **Maximum phases:** If $P=4$, then $F=C-P+2=1-4+2=-1$
Which is meaningless. Hence all the four phases cannot exist.

(iii) **Areas :** Four areas containing one phase each

(iv) **Curves:** There are six stable curves.

- a) Sublimation curve of S_R
- b) Sublimation curve of S_M

Phase Equilibrium

- c) Vapour pressure curve of S_L
- d) Transition curve of S_R
- e) Melting curve of S_M
- f) Melting curve of S_R

Meta stable curves: There are four metastable curves

- a) Sublimation curve of S_R
- b) Sublimation curve of S_M
- c) Vapour pressure curve of S_L
- d) Melting curve of S_R

Phase Equilibrium

Triple points:

There are three stable triple points S_R - S_M - S_V ,
 S_M - S_L - S_V , S_R - S_M - S_L and one metastable triple point S_R - S_L - S_V .